

UNDERSTANDING SURFACE PROCESSES ON MARS THROUGH STUDY OF IRON OXIDES/OXYHYDROXIDES: CLUES TO SURFACE ALTERATION AND AQUEOUS PROCESSES.

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We are performing oxidation and reduction reactions on hydrated ferric oxide minerals in order to investigate how these might alter under a variety of conditions on the surface of Mars. Preliminary experiments on ferrihydrite and goethite showed that heating these minerals in a dry oxidizing environment produces fine-grained hematite, while heating these minerals in a reducing environment produces fine-grained magnetite. Under Mars-like oxidation levels this magnetite then oxidizes to maghemite. These reactions are dependent on the presence of water and organic material that can act as a reductant. We are using reflectance and Mössbauer spectroscopy to characterize the reaction products and TEM to analyze the sample texture. Our preliminary results indicate that magnetite and maghemite could be formed in the soil on Mars from ferrihydrite and goethite if organics were present on early Mars.

Introduction: Ferrihydrite and goethite frequently form in aqueous terrestrial environments and may have formed on Mars if water was present. However, goethite contains OH and ferrihydrite contains both OH and H₂O, which might make these minerals unstable on the surface of Mars today. Investigating alteration of ferrihydrite and goethite enables us to understand what to look for today if these minerals formed on early Mars and subsequently altered. Aqueous alteration of ferrihydrite results in goethite or hematite, and high temperature alteration of goethite or ferrihydrite results in hematite [1]. Alteration under lower temperatures and in the presence of a reductant forms magnetite and maghemite [2]. Alteration experiments are underway in the lab on synthetic ferrihydrite and goethite samples through low-temperature heating experiments under various oxidizing and reducing conditions.

Low-temperature alteration experiments: Synthetic ferrihydrite and goethite samples were heated at a rate of 10 °C/min. using differential thermal analysis (DTA). Samples were run in air, 99.8% N₂ and 99.998% N₂ and differences were observed depending on the amount of oxygen present. Material was collected from the DTA reactions for reflectance and Mössbauer spectroscopy and TEM analyses. The texture of the samples are shown in Fig. 1 where small pockets of fine-grained crystalline material are observed in the altered

ferrihydrites. Experiments are underway on larger sample quantities, and the products will also be characterized by transmittance and emission spectra.

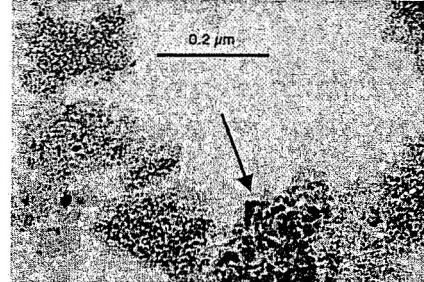


Figure 1. TEM image of altered ferrihydrite (432). This image shows the presence of a dominant amorphous phase (ferrihydrite and/or others) plus a less abundant crystalline phase (indicated by arrow).

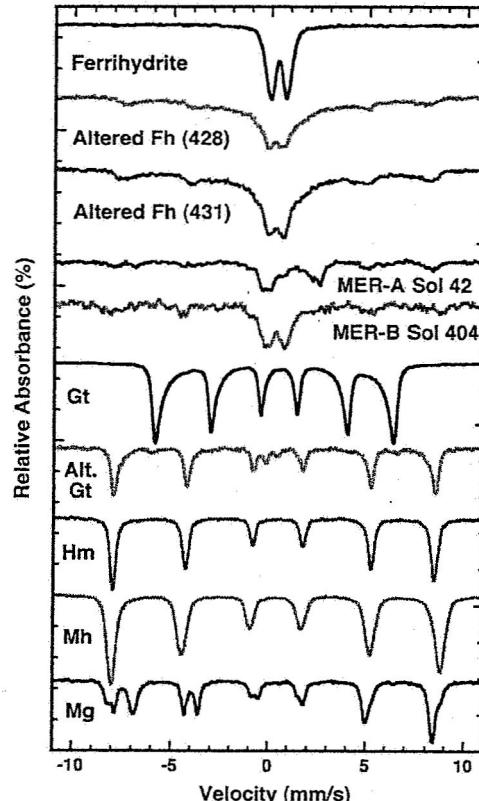


Figure 2. Mössbauer spectra (295 K) of altered ferrihydrite and goethite compared with iron oxide minerals and Martian soils (260-270K) from Gusev crater and Meridiani Planum.

Mössbauer characterization: Mössbauer spectra (Fig. 2) show changes in the ferrihydrite and goethite samples with alteration. The majority of the Fe in the altered ferrihydrates is Fe^{3+} in unreacted ferrihydrite and an amorphous phase. The poorly resolved magnetic phases are best fit with a combination of three sextets due to magnetite, maghemite, and goethite. The altered goethite (438) has been completely replaced with a combination of hematite and a small amount of a (probably Fe^{3+}) paramagnetic phase, possibly amorphous material. We are hoping to clarify these phases with low temperature measurements.

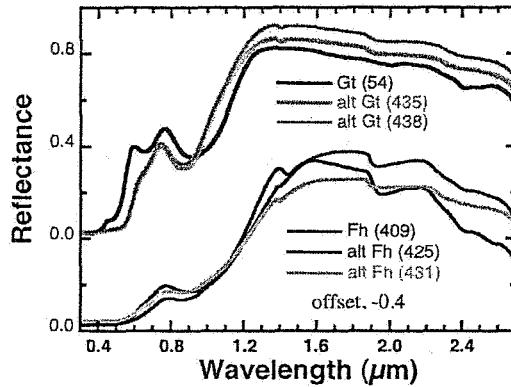


Figure 3. VNIR spectra of altered goethite and ferrihydrite showing differences upon heating with (431, 438) and without organic reductants (425, 435).

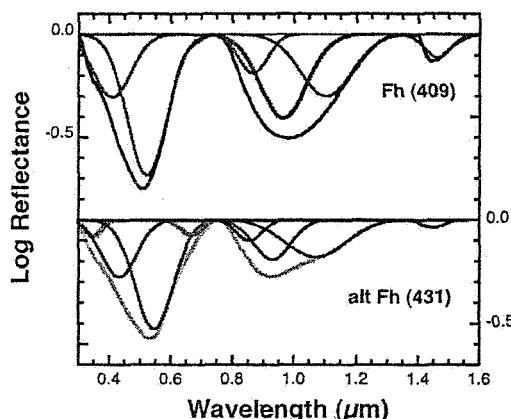


Figure 4. Continuum-removed spectra of ferrihydrite and altered ferrihydrite modeled with Gaussians. The band near $1.1\mu\text{m}$ is enlarged due to magnetite formation and additional bands are observed (pink) that are consistent with goethite.

Reflectance spectroscopy: Visible/near-infrared (VNIR) spectra are shown in Fig. 3. These spectra exhibit changes in the Fe bands and water/OH bands in this region. Subtle differences are also observed between the pure N_2 reactions and $0.2\% \text{O}_2$ reactions. In order to examine changes in the VNIR region in detail a continuum was removed and the spectra were fit to Gaussians as described in [3]. Examples are

shown in Fig. 4 for ferrihydrite and an alteration product. Changes in the number and strength of bands are due to reaction of the ferrihydrite sample and formation of new iron oxide phases.

Mid-IR spectra of fine-grained hydrated iron oxide minerals such as ferrihydrite and goethite are shown in Fig. 5 and exhibit features between $1200-1700\text{ cm}^{-1}$ ($\sim 5-8\text{ }\mu\text{m}$) that are not well understood. We are hoping that our experiments will enable better characterization of these features and perhaps also help explain the puzzling mid-IR doublet observed in this region for the Martian soils [4,5]. Differences are observed in this region for natural and synthetic ferrihydrite samples. Preliminary alteration experiments have also shown changes in these features for both ferrihydrite and goethite.

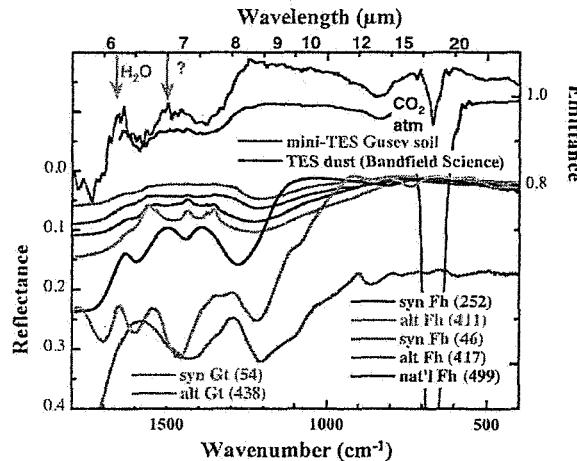


Figure 5. Mid-IR spectra of several ferrihydrite and goethite samples, plus alteration products. Emission spectra of Mars are shown for comparison [4,5].

Applications to Mars: Our lab experiments are designed to test plausible reactions of hydrated iron oxide minerals on Mars in an effort to identify the current iron oxide bearing minerals present there, as well as to understand minerals present earlier and the alteration history of the planet. The ferrihydrite and goethite features between $1200-1700\text{ cm}^{-1}$ vary in our preliminary reactions, so we are hopeful that future work will help explain the doublet observed near $1400-1650\text{ cm}^{-1}$ in Martian soil spectra.

References: [1] Cornell R. & U. Schwertmann (1996) *The Iron Oxides*, VCH, New York. [2] Campbell A. et al. (1997) *Clay Miner.* 32, 615. [3] Parente, M. & J. L. Bishop (2006) LPSC, submitted. [4] Bandfield J. L. et al. (2003) *Science*, 301, 1084. [5] Christensen P. R. et al. (2004) *Science*, 305, 837.

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